Inorganica Chimica Acta, 218 (1994) 139–142

New heptacoordinated tin complexes of 2,6-diacetylpyridinebis(thiosemicarbazone), H_2daptsc, and of 2,6-diacetylpyridinebis(semicarbazone), H_2dapsc. Crystal and molecular structures of [MeSnCl(Hdaptsc)]Cl·MeOH and [MeSnCl(H_2dapsc)]Cl_2·$2H_2O$

Gerimário F. de Sousa and Carlos A.L. Filgueiras*
Departamento de Química, ICEx, Universidade Federal de Minas Gerais, 31270 Belo Horizonte, MG (Brazil)

Anuar Abras
Departamento de Física, ICEx, Universidade Federal de Minas Gerais, 31270 Belo Horizonte, MG (Brazil)

Salih S. Al-Juaid, Peter B. Hitchcock and John F. Nixon
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (UK)

(Received August 27, 1993; revised December 13, 1993)

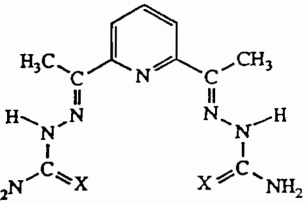
Abstract

Two new heptacoordinated organotin complexes, [MeSnCl(Hdaptsc)]Cl·MeOH (**1**) and MeSnCl(H_2dapsc)]Cl_2·$2H_2O$ (**2**), have been prepared from $MeSnCl_3$ and H_2daptsc and H_2dapsc, respectively. Single crystal X-ray diffraction studies showed them to be approximately pentagonal bipyramidal (PBP), with the organic ligands lying in the equatorial plane. H_2daptsc and $SnCl_4$ form a complex with the formula [ClSnCl(Hdaptsc)]Cl (**3**), which is presumed to have an analogous PBP structure. On the other hand, the complex obtained from H_2dapsc and Me_2SnCl_2 is tentatively formulated as [$(Me_2SnCl_2)_2$(H_2dapsc)] (**4**), and ^{119}Sn Mössbauer spectroscopic evidence suggests an octahedral coordination for the two tin atoms.

Key words: Crystal structures; Tin complexes; Polydentate ligand complexes; Thiosemicarbazone complexes; Chelate complexes

Introduction

2-Formylpyridine thiosemicarbazone (HFPT) has aroused great interest as a versatile ligand capable of forming complexes of remarkable biological activity and hexacoordinate tin complexes of this ligand were recently described [1]. The present work deals with the preparation of related complexes with the ligands 2,6-diacetylpyridinebis(thiosemicarbazone), H_2daptsc, and 2,6-diacetylpyridinebis(semicarbazone), H_2dapsc, whose structures are shown below.



X = S, O

These two ligands were chosen since they have the potential to form pentacoordinate or higher coordinated tin complexes. Furthermore different possibilities of keto–enol tautomerism make a comparison between the two ligands even more interesting.

Experimental

H_2daptsc·HCl and H_2dapsc·HCl were prepared in quantitative yield from 2,6-diacetylpyridine and the corresponding semicarbazide hydrochloride according to a modification of a process reported in the literature [2]:

$$2,6\text{-}(MeCO)_2py + H_2NNHCXNH_2 \cdot HCl \xrightarrow[\text{reflux}]{\text{EtOH}} \begin{array}{l} H_2\text{daptsc} \cdot HCl\ (X=S) \\ H_2\text{dapsc} \cdot HCl\ (X=O) \end{array}$$

---

*Author to whom correspondence should be addressed.

SSDI 0020-1693(94)03798-S

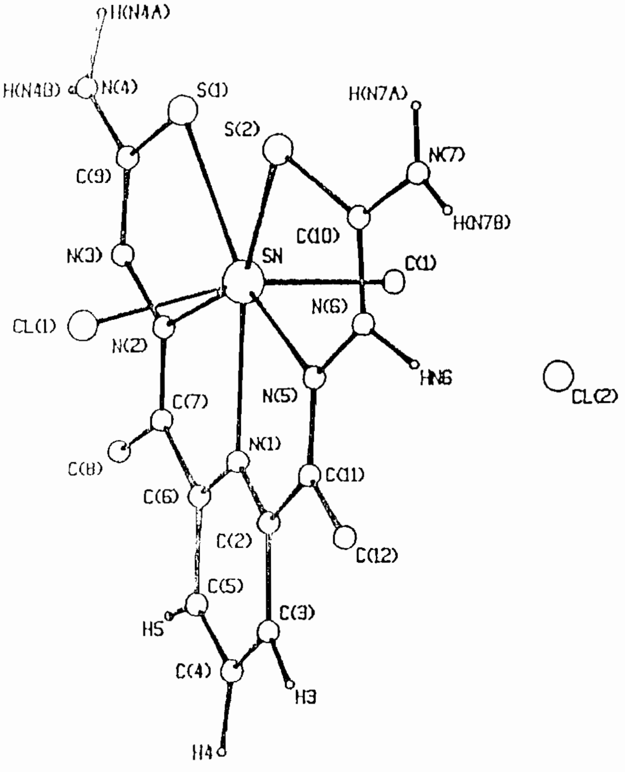


Fig. 1 Molecular structure of [MeSnCl(Hdaptsc)]Cl.

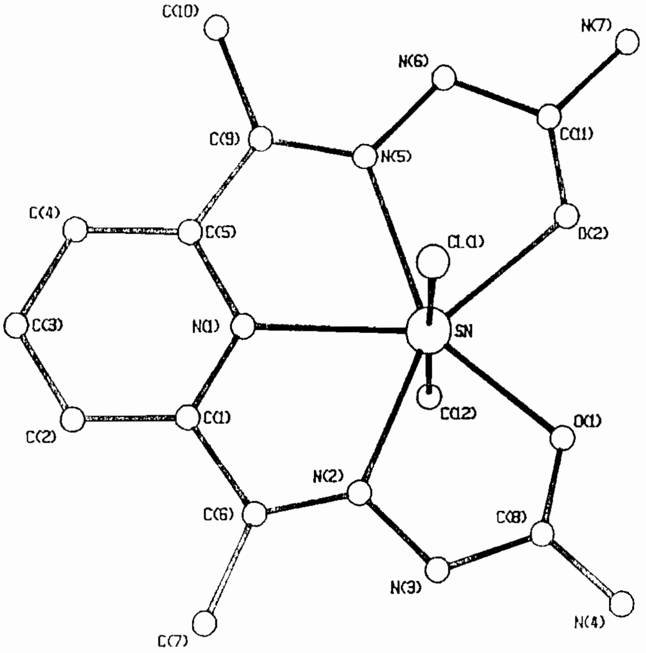


Fig. 2. Molecular structure of [MeSnCl(H_2dapsc)]Cl_2.

The complexes **1**–**4** were prepared by the following procedure. 0.21 mmol of the ligand (as the hydrochloride) were dissolved by refluxing for 20 min in dry MeOH. To this solution were added 0.24 mmol of the appropriate tin species dissolved in 5 ml of MeOH, and the resulting mixture was refluxed for 1 h, except for the $SnCl_4$ derivative, which precipitated immediately. Cooling the solution and slowly evaporating the solvent led to the appearance of crystalline products with yields of the order of 80%, which did not melt up to 250 °C. C, H and N analyses gave the following results:

1: Found: C, 27.8; H, 3.2; N, 18.4. Calc. for $C_{12}H_{17}Cl_2N_7S_2Sn \cdot CH_3OH$: C, 28.1; H, 4.0; N, 18.0%.

2: Found: C, 27.0; H, 3.7; N, 17.3. Calc. for $C_{12}H_{22}Cl_3N_7O_4Sn \cdot 2H_2O$: C, 26.0; H, 4.0; N, 17.7%.

3: Found: C, 24.2; H, 2.7; N, 13.8. Calc. for $C_{11}H_{14}Cl_3N_7S_2Sn$: C, 24.8; H, 2.6; N, 13.4%.

4: Found: C, 25.3; H, 3.7; N, 13.9. Calc. for $C_{15}H_{27}Cl_4N_7O_2Sn_2$: C, 25.1; H, 3.8; N, 13.7%.

^{119}Sn Mössbauer spectra were recorded using a constant acceleration spectrometer moving a $CaSnO_3$ source at room temperature. The samples were analysed at 85 K. All spectra were computer-fitted assuming Lorentzian single lines.

Due to poor solubility of the complexes, it was only possible to obtain the ^{119}Sn NMR spectrum of complex **1** in MeOH using a 300 MHz Bruker spectrometer.

The molecular structures of complexes **1** and **2**, established by single crystal diffraction studies, are shown in Figs. 1 and 2.

Results and discussion

Analytical data suggested loss of HCl in the formation of complexes **1** and **3**, but not in the other cases. This is corroborated for **1** and **2** by the crystallographic data*, and Figs. 1 and 2 show their molecular structures.

---

*Crystal data for **1**: $C_{12}H_{17}Cl_2N_7S_2Sn \cdot CH_3OH$, $M = 545.1$, monoclinic space group $P2_1/c$, $a = 11.868(10)$, $b = 11.257(14)$, $c = 15.911(11)$ Å; $\beta = 111.26(6)$, $U = 1980.9$ Å^3, $Z = 4$, $D_{calc} = 1.83$ g cm^{-3}. Monochromated Mo Kα radiation $\lambda = 0.71069$ Å, $\mu = 17.9$ cm^{-1}. The structure of the crystal (0.2 × 0.2 × 0.1 mm) was solved by routine heavy atom techniques and refined by full-matrix least-squares methods with non-H atoms anisotropic, using Enraf-Nonius Molen programs. Hydrogen atoms were located on a difference map and their positions refined with forced isotropic thermal vibration parameters, except the hydrogens of the Me group and the MeOH group which were omitted. 2180 significant reflections with $|F^2| > 3\sigma(F^2)$ were used in the refinement, which converged at $R = 0.044$ and $R' = 0.052$.

Crystal data for **2** $C_{12}H_{22}Cl_3N_7O_4Sn$, $M = 553.4$, monoclinic space group $P2_1/n$, $a = 9.024(5)$, $b = 13.485(3)$, $c = 17.297(2)$ Å; $\beta = 93.54(3)$, $U = 2100.8$ Å^3, $Z = 4$, $D_{calc} = 1.75$ g cm^{-3}. Monochromated Mo Kα radiation $\lambda = 0.71069$ Å, $\mu = 16.4$ cm^{-1}. The structure of the crystal (0.2 × 0.1 × 0.05 mm) was solved by routine heavy atom techniques and refined by full matrix least-squares methods, using Enraf-Nonius SDP programs with non-H atoms anisotropic. Me and H_2O H atoms were not located and were omitted. Other H atoms were fixed at calculated positions with $U_{iso} = 1.3U_{eq}$ for the parent atom. 2419 significant reflections with $|F^2| > 2\sigma(F^2)$ were used in the refinement, which converged at $R = 0.050$ and $R' = 0.061$.

During the formation of **1** the ligand H_2daptsc loses a proton and $MeSnCl_3$ loses two chloride ions, one as HCl, and the second chloride becomes the complex counter ion. The deprotonated complexed ligand, Hdaptsc, has one sulfur atom in the thione form and the other as a thiolate. The cationic complex forms a distorted pentagonal bipyramid (PBP), with the ligand acting as a pentadentate species lying in the equatorial plane containing the Sn atom, and Cl and Me occupy apical positions. The chloride counter ion forms weak hydrogen bonds with the N(6), N(7a) and N(7b) hydrogens of the coordinated ligand.

The ^{119}Sn NMR spectrum of **1** in MeOH gave the expected high field singlet at −510 ppm relative to Me_4Sn, indicative of considerable shielding of the tin nucleus, and a high coordination number, consistent with literature data for heptacoordinated tin compounds [3].

In an ideal PBP structure the five ligand atoms bonded to Sn should form a star pattern with 72° angles, but the actual angles are: S(1)–Sn–S(2) = 76.75(7), S(1)–Sn–N(2) = 75.8(2), S(2)–Sn–N(5) = 71.5(2), N(1)–Sn–N(2) = 69.7(2), N(1)–Sn–N(5) = 65.2(2)°. It is interesting to consider the difference between the angles S(1)–Sn–N(2) and S(2)–Sn–N(5). The former is part of a ring in which the sulfur atom is in the thiolate form in which it has an enhanced basicity compared to the thione sulfur. The Sn–S(1) = 2.527(2) Å and Sn–N(2) = 2.288(6) Å distances in the first ring, and Sn–S(2) = 2.633(2) Å and Sn–N(5) = 2.430(6) Å in the second, are compatible with the different S–Sn–N angles. A similar situation exists in the rings formed by SnN(2)C(7)C(6)N(1) and SnN(5)C(11)C(2)N(1), where the N(1)–Sn–N(2) angle is 69.7(2)°, while N(1)–Sn–N(5) is 65.6(2)°, and the N(2)–Sn bond (2.288(6) Å) is longer than the N(5)–Sn bond (2.430(6) Å). The shorter N(2)–Sn distance, compared to N(5)–Sn, may also be viewed as a result of the thiolate form of sulfur in the ring containing S(1). The N(1)–Sn distance of 2.238(6) Å seems rather long for a pyridine nitrogen bonded to Sn(IV), and in related structures the Sn–N (pyridine) distance was found to be 2.225(3) [1] and 2.307(4) Å [4], respectively. The slightly longer Sn–N distance in **1** may result from the geometric requirements of the structure, in which tin bonds to the two imine nitrogens, as well as to the pyridine nitrogen, preventing a closer approach of the latter to the metal.

The Sn–Cl(1) distance of 2.476(2) Å is similar to that found in the heptacoordinated Sn(IV) complex [BuSnCl(dapa)] (H_2dapa = 2,6-diacetylpyridinebis(2-aminobenzoylhydrazone)), where the Sn–Cl distance is reported as 2.446(3) Å [5]. The Sn–C(1) distance of 2.166(8) Å in our complex agrees with literature data for [BuSnCl(dapa)] (Sn–C = 2.138(20) Å) [5] and [Et_2Sn(dapt)] (Sn–C = 2.122(23) Å) (H_2dapt = 2,6-diacetylpyridinebis(2-thenoylhydrazone)) [3].

Complex **2** likewise was shown by single crystal X-ray crystallography to contain a distorted PBP dication, although the distortion is less than in **1**. The methyl group and a chlorine atom also occupy the axial positions and the ligand lies in the equatorial plane. Unlike **1**, however, which is a monocation, complex **2** contains a dication and chloride ions outside the coordination sphere, indicating no deprotonation of the ligand. Complex **2** is structurally similar to $[Sn(H_2dapsc)Cl_2]Cl_2 \cdot 2H_2O$, which has been described in the literature [6].

In **2** the angles along the equatorial plane are: O(1)–Sn–O(2) = 80.2(2), O(1)–Sn–N(2) = 70.7(2), O(2)–Sn–N(5) = 70.8(2), N(1)–Sn–N(2) = 68.8(2), N(1)–Sn–N(5) = 68.6(2)°, respectively. The deviation from the regular pentagonal angle of 72° parallels that in **1**, i.e. the angle X–Sn–X (X = S or O) is the largest, with X–Sn–N > N–Sn–N arising from constraints imposed by the ligand. Considering the rings involving Sn, namely O(1)SnN(2)N(3)C(8) and O(2)SnN(5)N(6)C(11), the angles O(1)–Sn–N(2) and O(2)–Sn–N(5) are almost the same, in accordance with the equivalence of the two CO groups, unlike the CS groups in **1**. The distances Sn–O(1) = 2.177(6) Å and Sn–O(2) = 2.180(6) Å, as well as C(8)–O(1) = 1.266(10) Å and C(11)–O(2) = 1.266(10) Å, also point to the equivalence of the two CO groups. The other two rings in **2**, N(1)SnN(5)C(9)C(5) and N(1)SnN(2)C(6)C(1), also contain two equivalent angles, N(1)–Sn–N(5) = 68.6(2)° and N(1)–Sn–N(2) = 68.8(2)°, unlike the situation prevailing in **1**. The N(2)–Sn = 2.284(7) Å and N(5)–Sn = 2.252(7) Å distances are also similar, reflecting the higher symmetry of this complex. The Sn–N(pyridine) distance, N(1)–Sn = 2.262(2) Å, is slightly shorter than in **1**, suggesting a somewhat stronger interaction.

The axial distances, Sn–Cl(1) = 2.386(2) Å and Sn–C(12) = 2.122(9) Å, are also shorter than their counterparts in **1**, whereas the angle Cl(1)–Sn–C(12) = 177.9(3) Å is much closer to 180° than in **1**.

Elemental analysis of **3** suggests its molecular composition to be [ClSnCl(Hdaptsc)]Cl_2, indicating that its structure might be similar to that of **1**, with two chlorine atoms lying in the axial positions of the presumed PBP. Unfortunately it was not possible to obtain single crystals for X-ray crystallography due to its insolubility in all solvents tested.

The bimetallic complex **4**, which was shown by analysis to be $[(Me_2SnCl_2)_2(H_2dapsc)]$, also did not produce good single crystals; however, it seems to be a totally different complex compared to the other three, from the following observations.

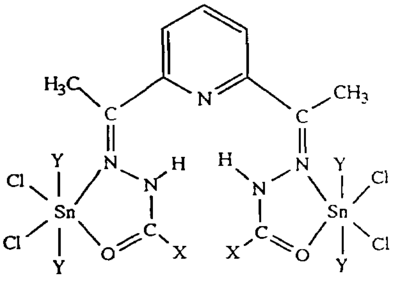
^{119}Sn Mössbauer spectroscopy was performed on all four complexes, giving the results shown in Table 1.

TABLE 1. ^{119}Sn Mossbauer parameters

Compound	δ (mm s^{-1})	Δ (mm s^{-1})
[MeSnCl(Hdaptsc)]Cl·MeOH (**1**)	0.97	2 16
[MeSnCl(H_2dapsc)]Cl_2·$2H_2O$ (**2**)	0 68	2.15
[ClSnCl(Hdaptsc]Cl (**3**)	0.61	0.66
[(Me_2SnCl_2)$_2$(H_2dapsc)] (**4**)	1.43	4.36
[BuSnBu(daps)]^a (**5**)	1.27	3.73
[BuSnCl(dapt)]^a (**6**)	0.75	1.80
[Me_2SnCl_2·$(DMSO)_2$]^b (**7**)	1 38	4 18

^{a}Ref. 3, H_2daps = 2,6-diacetylpyridinebis(salicyloylhydrazone), H_2dapt = 2,6-diacetylpyridinebis(2-thenoylhydrazone) ^{b}Ref. 6.

Complexes **1** and **2** gave similar isomer shifts (δ) and quadrupole splittings (Δ), which also agree with the data for complex **6**, whose structure has been established as a PBP [3]. The inverse dependence of δ with the electronegativity of the substituents is shown when one compares **5** and **6**. A similar situation is seen in **1** and **2**, and the effect of the negative charge in Hdaptsc$^-$ may also account for the higher δ value of **1** compared to **2**. In **3** the replacement of one methyl group by chlorine leads to the expected lower δ value. Variation in the quadrupole splittings, Δ, which are dependent upon the deviation of electronic charge distribution from a cubic symmetry, are more difficult to rationalise. Complex **7** is a known hexacoordinate Sn species [7] whose Mössbauer parameters are remarkably close to those of complex **4** and these data suggest that the latter might be a bimetallic compound in which both Sn atoms are six-coordinate. Moreover, the Mossbauer spectrum shows the presence of only one kind of Sn atom, indicating the equivalence of the two metal centres. Thus **4** is tentatively postulated as having the following structure.



$X = NH_2$, $Y = CH_3$

Supplementary material

All other intramolecular distances and angles as well as atomic and thermal parameters are available from the authors on request.

Acknowledgements

The authors are grateful for research support from CNPq and Fapemig in Brazil, as well as for a CNPq scholarship to G.F.S.

References

1 R.S Barbieri, H.O. Beraldo, C.A.L. Filgueiras, A. Abras, J.F. Nixon and P.B Hitchcock, *Inorg Chim Acta, 206* (1993) 169

2 G.J. Palenick, D.W. Wester, U. Rychlewska and R.C. Palenick, *Inorg Chem., 15* (1976) 1814.

3 C. Carini, G. Pelizzi, P. Tarasconi, C. Pelizzi, K C. Molloy and P.C. Waterfield, *J Chem Soc, Dalton Trans,* (1989) 289.

4 G.F. de Sousa, C A.L Filgueiras, M.Y. Darensbourg and J.H. Reibenspies, *Inorg Chem, 31* (1992) 457.

5 C. Pelizzi, G. Pelizzi and G. Predieri, *J. Organomet. Chem., 263* (1984) 9.

6 S.O. Sommerer and G.J. Palenik, *Inorg Chim Acta, 183* (1991) 217

7 A.J. Crowe and P.J. Smith, *J Organomet Chem, 224* (1982) 223.